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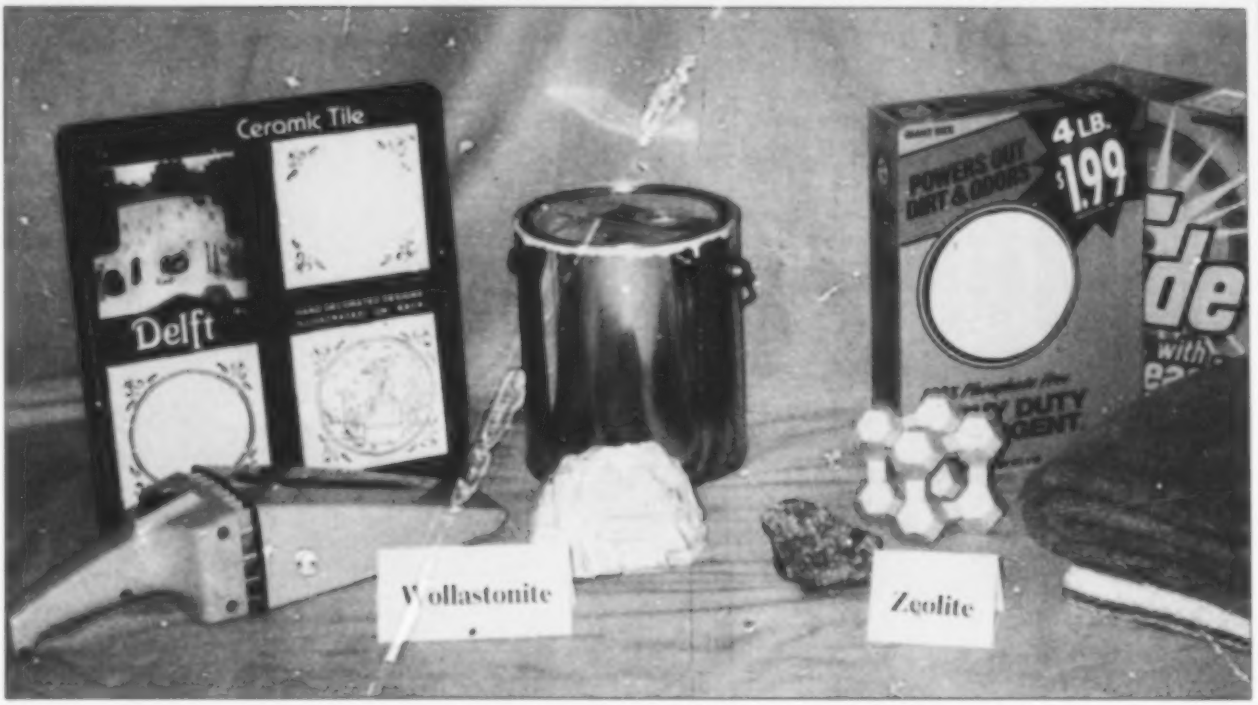

WOLLASTONITE AND ZEOLITES

By Michael J. Potter and Robert L. Virta

1990

U.S. DEPARTMENT OF THE INTERIOR

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ANNUAL REPORT

WOLLASTONITE AND ZEOLITES

U.S.
DEPARTMENT
OF THE
INTERIOR

Manuel Lujan, Jr.
Secretary

BUREAU
OF
MINES

T S Ary
Director

September 1991

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COVER PHOTO
Wollastonite is used as a filler in ceramic tile, paint, and plastics and has applications as an asbestos substitute in insulation board, cement, tile, and brakes. Synthetic zeolites are used in phosphate-free or low-phosphate detergents in place of sodium tripolyphosphate. The synthetic zeolite conditions the wash water by removing calcium and magnesium ions.

For comments or further information, please contact
The Branch of Industrial Minerals
The Division of Mineral Commodities
U.S. Bureau of Mines
2401 E St., NW, MS 5209
Washington, DC 20241-0001
Telephone: (202) 634-1185 (Wollastonite) or (202) 634-1206 (Zeolites)
Fax: (202) 634-4091

WOLLASTONITE AND ZEOLITES

By Michael J. Potter and Robert L. Virta

Mr. Potter, a physical scientist with 24 years of industry and U.S. Bureau of Mines experience, has been the commodity specialist for wollastonite since 1976. Domestic survey data were prepared by Pam Shorter, mineral data assistant.

Mr. Virta, a physical scientist with 15 years of U.S. Bureau of Mines experience, has been the commodity specialist for natural zeolites since 1986. Domestic survey data were prepared by Maureen Riley, mineral data assistant.

WOLLASTONITE

Wollastonite is natural calcium silicate and has a theoretical composition of $CaO \cdot SiO_2$. It has developed a significant role as a high-performance mineral filler in paint, plastics, and thermal board. It is used in asbestos replacement and in ceramics such as wall tile, where it promotes low shrinkage, good strength, low warpage, and fast firing.

After preliminary drilling of an extensive wollastonite deposit on the Gilbert properties near Tonopah, NV, Sikaman Gold Resources Ltd. was considering a proposed followup drilling program to prove a minimum of 2 million tons grading more than 50% wollastonite. If successful, this would be followed by a further expenditure for detailed reserve definition, extensive sample testing, and market evaluation. In late 1990, ownership of the Gilbert properties remained uncertain. During early 1990, Vancouver-listed White Plains Resources Corp. purchased a 25% stake in the properties from Sikaman. In mid-1990, White Plains raised its option to 100% by intending to purchase Sikaman's remaining 75% interest in the properties.[1]

Domestic sold and used data for wollastonite were developed by the U.S. Bureau of Mines by means of a voluntary survey. Both active operations responded, representing 100% of the total canvassed. Specific data were withheld to avoid disclosing company proprietary data.

The two U.S. producers were NYCO, a division of NYCO Minerals Inc., Essex County, NY, and R. T. Vanderbilt Co. Inc., Lewis County, NY. The tonnage of wollastonite sold or used in 1990 decreased compared with that of the previous year.

Wollastonite is used as a filler in ceramic tile, paint, and plastics. It serves as an asbestos replacement in some applications such as a reinforcement filler for boards and panels in various heat containment applications, including ovens, dryers, thermal ducting, and many other thermal applications. Wollastonite also replaces asbestos in certain cement formulations, in ceilings and floor tile, and in friction applications such as brake linings.

Prices from Industrial Minerals, December 1990, for wollastonite, exworks, converted to dollars per metric ton, were approximately $278 to $292 for acicular, minus 200 mesh; $193 to $204 for minus 325 mesh; and $209 to $215 for minus 400 mesh. Prices per metric ton for wollastonite, f.o.b. plant, bulk, were $125 to $177 for 200 mesh and $235 for 325 mesh.

In Canada, a joint venture between Cominco Ltd. and Platinova Resources Ltd. continued to assess the Deloro wollastonite property near Marmora, Ontario, halfway between Toronto and Ottawa. Four zones had been outlined, with the grade of wollastonite ranging from 28% to 60%. The mineralization consisted of calcite-wollastonite-diopside marbles. Wollastonite concentrates were obtained by cofloating wollastonite and diopside from calcite and then magnetically separating diopside from the wollastonite. Both companies were reassessing calcite and wollastonite markets and conducting further tests to optimize products.

Another wollastonite project involved Ram Petroleums Ltd.'s evaluation of a deposit at Mount Grove in eastern Ontario. Drilling in late 1990 had proved 2.8 million tons of ore grading an average of 35% wollastonite with calcite and minor diopside. Laboratory work was being carried out.

In British Columbia, Performance Minerals of Canada Ltd. agreed to acquire a 50% working interest in Tri-Sil Minerals Inc.'s Wormy Lake wollastonite property about 45 kilometers northwest of Vancouver. Potential reserves were estimated to be more than 50 million tons. During the next 5 years, Performance Minerals was to prove up the reserves. Material tested down to minus 100 mesh showed high aspect ratios of 20:1 on average. A crushing plant was sizing low-grade wollastonite and selling it to Tilbury Cement of Richmond, British Columbia.

In the Yukon Territory, Archer, Cathro, & Associates discovered a deposit about 450 kilometers from the port town of Haines, AK. Surface grab samples indicated some material containing 60% and 80% to 85% wollastonite; but drilling of core samples had yet to be carried out.[2]

In China, wollastonite production in Jilin and Hubei Provinces was estimated to be at least 70,000 tons per year. In Yunnan Province, a deposit was reportedly discovered in early 1989 containing an estimated 50 million to 100 million tons of reserves. If proven, this would represent the world's largest wollastonite deposit.

Domestic consumption probably accounted for the bulk of the wollastonite

produced in China. Wall tile was the major end use, but increasing quantities were being used in other applications such as pigments, paper and plastic fillers, ceramics and porcelains, electrode coatings, and other uses. The most rapid increase in consumption was in steelmaking, where wollastonite is used as a protective slag for continuous casting carbon steel and for casting silicon steel sheet.

Exact figures for total annual wollastonite exports from China were not available. However, exports in 1985 from the Jilin branch of the China Metallurgical Imports and Export Corp. were an estimated 36,000 tons.[3]

In Greece, Metallic & Industrial Minerals Mevior SA of Thessaloniki was developing a wollastonite deposit in Kimmeria. The deposit contained 300,000 tons of 60% to 70% wollastonite and 10% calcite. Construction of a 500-ton-per-year pilot plant was to begin in late 1990.

In Mexico, Cia Minera Constelacion S.A. de C.V., an affiliate of Cominco Resources International Ltd., continued to develop the San Martin wollastonite deposits about 50 kilometers northwest of Hermosillo in the State of Sonora. Drilling was being carried out in the South Body, which contains 0.7 million tons grading 70% wollastonite. Mineralization consisted of wollastonite-calcite-quartz-diopside marble. Some hand-sorted material was ground into test quantities of powder and acicular grades suitable for the ceramics, plastics, and coatings markets. Marketing studies were underway, and a small-scale production test was being planned.

In the Republic of South Africa, the country's first commercial wollastonite operation appeared ready to come on-stream in early 1991. Pella Refractory Ores' mine at Modderfontein, 18 kilometers northeast of Garies in Namaqualand, contained in excess of 2 million tons. The ore, containing 50% to 60% wollastonite, requires a complex three-stage beneficiation process, including electrostatic and high-intensity magnetic separation and flotation, to give a product containing more than 90% wollastonite. An output of 13,600 tons per year of wollastonite was anticipated from treating 72,000 tons per year of ore.

Initial production was slated to be about 500 tons per month, increasing to 1,000 tons per month as markets develop. Two grades would be produced for the ceramics and asbestos replacement markets. Much of the output would be exported.[4]

Research on the synthesis of B-wollastonite (synthetic wollastonite) was performed. Highly reactive silica such as diatomite was used, important deposits of which occur in Spain. Other silica materials were also used for comparison, such as quartz and silica gel. In the whiteware industry, modern fast-firing technology has almost fully replaced traditional double firing, resulting in high energy savings. B-wollastonite is one of the raw materials suitable for compositions to be fast fired because of the good characteristics it gives to ceramic bodies, such as low drying and low firing shrinkage, high bending strength, etc.[5]

A paper described the surface modification of silica and silicate minerals by silanes, on which Quartzwerke GmbH has done development work and has commercialized since the early 1970's. A variety of silanes are used to coat silica flour, cristobolite, wollastonite, alumina trihydrate, and calcined clay.

The company's TREMIN-wollastonite (silane-treated wollastonite) is used in the improvement of polyamide, polypropylene, and polyurethane engineering resins as well as fluorosilicone elastomers. TREMIN-wollastonite used in polyamide compounds in the automotive industry adds toughness and impact strength to the polymer. It may be used partially to replace glass fiber reinforcement without loss of strength and stiffness of the composite. TREMIN-wollastonite can also be employed in fluoroelastomers instead of carbon black.[6]

The outlook appears to be favorable for wollastonite, especially in fine particle size, high aspect ratio, and chemically modified grades.

The plastics market is one area of further potential growth. Chemically treated grades of wollastonite are increasing by being required to satisfy customer and product requirements. In the United States, plastics consumption has been affected by reduced activity in two major markets, construction and automobiles. However, plastic consumption in Europe in 1990 was at a high level.

Wall tile has been a major end use of wollastonite. U.S. consumption of tile increased during the past 10 years, including U.S. output and imports from Europe. In 1990, the U.S. remodeling market was strong, although the construction industry was experiencing a slowdown. European tile producers generally rely on cheaper lime, silica, and feldspar raw materials rather than on wollastonite for their wall tile bodies.

Asbestos replacement is a possible growth area because of a proposed ban in the United States on almost all asbestos-containing materials in stages during the next 7 years. Outside the United States, asbestos is being replaced to some extent by wollastonite in brake linings, gaskets, and products where short-fiber asbestos was previously used. If legislation should be taken up by authorities in Europe and Asia, prospects of a growing market for high aspect ratio wollastonite are good.[7]

ZEOLITES

Zeolites are hydrated aluminosilicates of the alkaline and alkaline-earth metals. Approximately 40 natural zeolites have been identified during the past 200 years, the most common of which are analcime, chabazite, clinoptilolite, erionite, ferrierite, heulandite, laumontite, mordenite, and phillipsite. Zeolites are commercially valuable because of their unique ion-exchange, molecular sieving, and catalytic properties.

Commercial zeolite deposits in the United States are associated with the alteration of volcanic tuffs in saline, alkaline lake deposits, and open hydrologic systems. The deposits are in Arizona, California, Idaho, Oregon, Nevada, New Mexico, Texas, and Utah. The major components of these deposits are chabazite, clinoptilolite, mordenite, and phillipsite. Erionite, orthoclase and plagioclase feldspar, montmorillonite, opal, quartz, and volcanic glass may be present in some deposits as minor components. The composition of these deposits was determined primarily by the temperature and pressure of formation and the chemistry of the altering fluids. When the alteration process went to completion, the zeolite content of portions of some deposits approached 100%.

Conventional mining techniques were used in the mining of natural zeolites. The overburden was removed to permit

access to the ore, and the ore was stripped for processing using front-end loaders or tractors equipped with ripper blades. The fractured ore was dried and then crushed using either jaw crushers or roller mills. The crushed ore was packaged directly for shipping or was screened to remove fine material when a granular product was required.

Nine companies mined or sold natural zeolites in the United States in 1990. Clinoptilolite was mined in California, New Mexico, Nevada, Oregon, Texas, and Wyoming. Chabazite was mined in Arizona. Total domestic production and sales were 15,569 metric tons (17,162 short tons) in 1990, an increase of 28% from those of 1989.

Natural zeolites were used for pet litter, odor control, animal feed supplement, desiccant, chemical carrier, aquaculture, wastewater cleanup, aquarium filters, gas adsorbent, water purification, and oil and/or grease adsorbent, in decreasing order of consumption. The properties that made natural zeolites commercially valuable included ammonium adsorption (aquaculture, aquarium filters, odor control applications, pet litter, and water purification), moisture adsorption (desiccants, odor control, and pet litter), and ion-exchange capabilities (wastewater cleanup).

Atlantic Richfield Co., Steelhead Specialty Minerals, and the Advanced Minerals and Hazardous Waste Processing Center for Excellence at Montana Tech investigated the use of clinoptilolite for removing heavy and toxic metals from mine water in a former copper mine in Montana. The mine water contained arsenic, copper, and zinc that potentially could contaminate the local ground water. Preliminary tests indicated that the heavy-metals content of the water could be reduced with the application of lime, but that the water did not meet drinking water standards. The partnership will perform tests to determine if the levels of heavy metals can be reduced further through an ion-exchange process using clinoptiliolite as the exchange media.[8]

The Montana Bureau of Mines and Geology received a grant for a 2-year study of the potential use of natural zeolites to remove metals from polluted waters and soils. The zinc content of one polluted water was reduced from 175 parts per liter to 0.02 parts per liter in a preliminary ion-exchange test.[9]

Mordenite, a natural zeolite, performed poorly as a shape-selective catalyst. It was rapidly deactivated during the reaction process. Researchers at Dow Chemical Co. modified the mordenite structure through an acid washing, calcining, and activation process to improve its performance as a shape-selective catalyst. The treatment increased the ratio of silicon to aluminum from 5:1 for the natural zeolite to 15:1 for the modified form of mordenite and increased the pore volume of the zeolite. The modified mordenite was suitable for use as a shape-selective catalyst for industrial applications such as the alkylation of biphenyl with propylene.[10]

Zeolites were fed to roosters and breeder hens in an effort to increase the strength of shells of eggs for market. The zeolite additive strengthened the shell strength by increasing the absorption of calcium. Researchers at Ethyl Corp. began feeding pigs, cows, and sheep zeolite as a feed additive to see if it improves bone strength and increases growth rates of the animals.[11]

Researchers at the University of California, Santa Barbara, studied molecular interactions on the surface of a zeolite by using an atomic force microscope. The study examined how positively charged t-butyl ammonium ions and neutral t-butanol molecules were bound to the surface of a zeolite that is used to remove ammonium and phosphate ions during wastewater treatment. Positively charged t-butyl ammonium ions occurred as clumps on the surface of the zeolite, while the neutral t-butanol molecules spread over the surface as a sheet. A better understanding of the molecular interactions that affect catalytic reactions was gained through the use of the atomic force microscope.[12]

Demand for synthetic zeolites for detergents continued to grow in Europe and the United States. Annual consumption in Europe was estimated to be 325,000 tons. Present U.S. demand was estimated to be 100,000 tons per year.[13] Manufacturers substituted synthetic zeolites for phosphates because phosphates promoted plant growth that degraded the quality of the water into which the phosphate-rich wastewater was released. Zeolites exchanged sodium for calcium and magnesium in the washwater much the same as the phosphate additives but at a slower rate. Fine grinding was used to enhance ion exchange and avoid visible zeolite deposition on clothes. Zeolite additives were nontoxic to marine and freshwater life.[14]

TABLE 1

DOMESTIC ZEOLITE PRODUCERS, 1990

State and company	Type of zeolite
Arizona:	
GSA Resources Inc.	Chabazite
NRG Inc.	Do.
UOP Inc.	Do.
Non Scents	Do.
California:	
Steelhead Resources Ltd.	Clinoptilolite
Idaho:	
Teague Mineral Products Co.	Do.
Nevada:	
East-West Minerals Inc.	Do.
Texas:	
Zeotech Corp.	Do.
Wyoming:	
U.S. Zeolites	Do.

[1]O'Driscoll, M. Wollastonite Production—Tempo Rises as Markets Grow. Ind. Miner. (London), No. 279, Dec. 1990, pp. 15, 19.

[2]Pages 17 and 19 of work cited in footnote 1.

[3]Roskill Information Services Ltd. (London). The Economics of Wollastonite 1990. 4th ed., 1990, pp. 26–27.

[4]Page 19 of work cited in footnote 1.

[5]Ibanez, A., J. M. Gonzalez Pena, and F. Sandoval. Solid State Reaction for Producing B Wollastonite. Am. Ceram. Soc. Bull., No. 69, No. 3, Mar. 1990, p. 374.

[6]Hofmann, F. A., and D. Skudelny. Surface Treated Mineral Fillers—Growing Markets for Specialty Products. Paper in 9th "Industrial Minerals" International Congress, ed. by J. B. Griffiths (Proc. Conf. Sydney, Australia, Mar. 25–28, 1990). Met. Bull. PLC, 1990, pp. 90–103.

[7]Pages 21–23 of work cited in footnote 1.

[8]The Miner's News. California Zeolites Studied for Role in Mine Drainage Cleanup at Montana's Berkeley Pit. Feb.–Mar. 1990, p. 9A.

[9]Great Falls (Montana) Tribune. Zeolites Studied for Mining Potential. Nov. 22, 1990.

[10]Haggin, J. Mordenite Used as Shape Selective Catalyst. Chem. & Eng. News, v. 68, No. 32, 1990, p. 29.

[11]Business Week. A New Chicken Feed That Arouses Roosters. No. 3173, Aug. 13, 1990, p. 120.

[12]Science News. High-Tech Microscope Makes Molecules Move. V. 137, No. 11, Mar. 17, 1990, p. 165.

[13]Chemical Week. Soaps and Detergents. V. 148, No. 4, Jan. 31, 1990, pp. 20–64.

[14]Dwyer, M., S. Yeoman, J. Lester, and R. Perry. A Review of Proposed Nonphoshate Detergent Builders, Utilisation and Environmental Assessment. Environ. Tech., v. 11, pp. 263–294.

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* U.S. Government Printing Office : 1991 - 281-985/40088